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SPECIFICATION

1. Title of the Invention

Fuel Oil Additive

2. Claims A fuel oil additive, characterized by being a copolymer of ethylene and a vinyl carboxylate, wherein at least 1/10 (molar ratio) of the vinyl carboxylate content of said copolymer is a vinyl ester of a carboxylic acid with a carbon number of 4 to 8, and the above-mentioned copolymer contains 2 to 20 mol% vinyl carboxylate, its number average molecular weight is 1500 to 5000, and it contains more than 6 alkyl branches per 100 methylene groups.

3. Detailed Description of the Invention

The present invention relates to an additive that is used to improve the clogging resistance of a fuel oil, and particularly an intermediate fraction fuel oil with a narrow boiling point range, whose boiling point is between 120 and 500°C and in which the difference between the 20% distillation temperature and the 90% distillation temperature is less than 100°C.

When a fuel oil is exposed to low temperatures, the wax contained in the oil precipitates as crystals, and when the oil is used as the fuel for a diesel engine, this precipitation clogs the filter and results in poor engine performance. In extreme cases, the oil solidifies in the fuel line and does not flow at all. Fluidity improvers are used in order to ameliorate these problems encountered at low temperatures, but while the improvers used at the current time do effectively improve fluidity and clogging resistance for intermediate fraction oils with a wide boiling point range, in which the difference between the 20% distillation temperature and the 90% distillation temperature is at least 100°C, they are unable to improve the clogging resistance of intermediate fraction oils in which the temperature difference is less than 100°C, although they do improve the fluidity of these oils.

An object of the present invention is to offer an improver capable of improving both fluidity and clogging resistance at the same time when added to an intermediate fraction fuel oil with a narrow boiling point range in which the difference between the 20% distillation temperature and the 90% distillation temperature is less than 100°C.

A copolymer of ethylene and a vinyl carboxylate is the best known low-temperature fluidity improver for fuel oils. According to Japanese Patent Publication 39-20669, the fluidity and clogging resistance of a fuel oil can be improved by using a copolymer of ethylene and a

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vinyl carboxylate with a carbon number of 3 to 5, wherein the vinyl carboxylate content is 1 to 40 wt% and the number average molecular weight is 700 to 3000. Examples of vinyl carboxylates are vinyl acetate with a carbon number of 4 and vinyl propionate with a carbon number of 5. However, when a copolymer such as this is added to an intermediate fraction fuel oil with a narrow boiling point range, it is possible to improve the fluidity but not the clogging resistance. To improve clogging resistance, it is believed that it is important for the additive to work as a nucleator when the wax is precipitating as crystals in the oil; but the solubility of the copolymer in the fuel oil when the carbon number of the alkyl groups in the carboxyl groups is small is inadequate for improving the clogging resistance of a fuel oil with a narrow boiling point range, and this is surmised to be the reason why there is no effect.

According to Japanese Patent Publication 48-23165, the fluidity and clogging resistance of an intermediate fraction fuel oil will be effectively improved by the use of a low temperature fluidity improver comprising a copolymer of ethylene and an unsaturated ester, or a copolymer of ethylene, an unsaturated ester, and an α -monoolefin, wherein the ethylene accounts for 3 to 40 mol% and the comonomer for 1 mol%, the number average molecular weight is 1000 to 2900, and said copolymer has 6 or fewer methyl end side chains per 100 methylene groups other than the methyl in the ester. However, when a copolymer such as this is used as a low temperature fluidity improver for an intermediate fraction fuel oil with a narrow boiling point range, in which the difference between the 20% distillation temperature and the 90% distillation temperature is less than 100°C, the fluidity is improved but not the clogging resistance. The reason for this is not clear, but is surmised to be that the number of methyl end side chains probably affects the solubility of the copolymer, and the solubility is inadequate for improving the clogging resistance of a fuel oil with a narrow boiling point range.

As discussed above, with technology available up to now, there was no known fluidity improver capable of effectively improving the clogging resistance of an intermediate fraction fuel oil with a narrow boiling point range.

Light oil is a typical example of an intermediate fraction fuel oil with a narrow boiling point range. The method that is generally employed at the present time to improve the clogging resistance of such a light oil is to mix in a kerosene fraction, which is a component with a lower boiling point. However, not only is this method disadvantageous from a cost standpoint, but it also leads to a reduction in the yield of kerosene, and as such is an industrially disadvantageous method. In light of this situation, if there were an effective improver for improving the clogging resistance of a light oil with a narrow boiling point range, it would be extremely valuable for industrial purposes.

The inventors conducted painstaking research aimed at finding a means for solving these problems. When an intermediate fraction fuel oil with a wide boiling point range is exposed to a low temperature and crystals of wax precipitate, there is a temperature difference of several degrees (°C) or more between the temperature at which the crystals begin to precipitate (the cloud point) and the temperature at which solidification occurs (the pour point), but in the case of an intermediate fraction fuel oil with a narrow boiling point range, this temperature difference is virtually absent, and once crystals of wax begin to precipitate, crystallization proceeds rapidly and the oil solidifies. Also, the temperature at which the precipitation of crystals begins tends to be lower with an intermediate fraction fuel oil with a narrow boiling point range. Meanwhile, when the mechanism by which a fluidity improver acts is considered, there seem to be two effects, that of a modifier of the wax crystal morphology, and that of a nucleator when the wax component precipitates as crystals. If this effect as a nucleator is effectively manifested, then numerous crystal precipitation sites are generated, the size of the crystals is naturally smaller, and the clogging resistance is improved. Therefore, the key to improving clogging resistance lies in how effectively this effect as a nucleator can be manifested. In the belief that the solubility of the copolymer used as a fluidity improver with respect to the fuel oil is at the crux of the solution in regard to an intermediate fraction fuel oil with a narrow boiling point range as discussed above, the inventors arrived at the present invention as a result of conducting research aimed at optimizing the molecular structure of various copolymers.

Specifically, the present invention is a fuel oil additive, characterized by being a copolymer of ethylene and a vinyl carboxylate, wherein at least 1/10 (molar ratio) of the vinyl carboxylate content of said copolymer is a vinyl ester of a carboxylic acid with a carbon number of 4 to 8, and the above-mentioned copolymer contains 2 to 20 mol% vinyl carboxylate, its number average molecular weight is 1500 to 5000, and it contains more than 6 alkyl branches per 100 methylene groups.

The additive of the present invention is excellent for improving the clogging resistance at low temperatures of a fuel oil that is an intermediate fraction fuel oil with a boiling point range of 120 to 500°C, and that has a narrow boiling point range in which the difference between the 20% distillation temperature and the 90% distillation temperature is less than 100°C.

The present invention will now be described in detail.

A vinyl ester of a carboxylic acid with a carbon number of 4 to 8 is suitable as the vinyl carboxylate used in the present invention. A vinyl ester of a carboxylic acid with a carbon number of 2 or 3 can be used if a vinyl ester of a carboxylic acid with a carbon number of 4 to 8 is also used, but in this case at least 1/10 (molar ratio) of the vinyl carboxylate in the copolymer must be a vinyl ester of a carboxylic acid with a carbon number of 4 to 8. If this

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ratio is less than 1/10, the clogging resistance of an intermediate fraction fuel oil with a narrow-boiling point range cannot be improved. Preferably, the molar ratio of the vinyl ester of a carboxylic acid with a carbon number of 4 to 8 should be at least 1/2, and even more preferably, the vinyl ester of a carboxylic acid with a carbon number of 4 to 8 is used alone.

Examples of vinyl carboxylates include vinyl butyrate, vinyl isobutyrate, vinyl valerate, vinyl isovalerate, vinyl pivalate, vinyl caproate, vinyl isohexanoate, and vinyl caprylate. The vinyl ester with a carbon number of 2 that can be combined with these vinyl carboxylates is vinyl acetate, and the one with a carbon number of 3 is vinyl propionate.

The vinyl carboxylate content in the copolymer of the present invention is between 2 and 20 mol%. A copolymer in which this content is below 2 mol% or over 20 mol% will have an inferior clogging resistance improving effect. A preferable content range is 3 to 15 mol%.

When the molecular weight of the copolymer is measured by vapor phase osmotic pressure method (VPO), the number average molecular weight will be between 1500 and 5000. If the number average molecular weight is below 1500, the copolymer will be extremely difficult to manufacture. On the other hand, if the number average molecular weight is over 5000 the copolymer will have inferior performance as a low temperature fluidity improver. A preferable range for the number average molecular weight is 2000 to 4500.

Another important factor that defines the copolymer is the number of alkyl branches present in the main chain of the copolymer. The alkyl branch number is measured by proton nuclear magnetic resonance (H^1 NMR). The ratio of the numbers of methyl groups and methylene groups is determined by said nuclear magnetic resonance, the number of end methyl groups is found by means of the number average molecular weight determined by VPO, the amount of methyl groups and methylene groups originating in the vinyl carboxylate is subtracted from the vinyl carboxylate content, and this difference is corrected to obtain the number of methyl groups per 100 methylene groups. The number of alkyl branches determined in this manner must be greater than 6. At 6 or less, the copolymer will not effectively improve clogging resistance. A preferable range for the number of alkyl branches is 6 [sic] to 10.

The copolymer is manufactured by radical polymerization. Favorable polymerization equipment is any ordinary equipment used for manufacturing high pressure polyethylene, and may be equipped with either a tank-type reactor or a tube-type reactor. The copolymerization is carried out under a pressure of 1000 to 3500 kg/cm² and at a temperature of 150 to 350°C in the presence of a free radical-forming catalyst and/or oxygen. A commonly known polymerization regulator can be used in order to control the molecular weight.

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The term "free radical-forming catalyst" refers to a known polymerization initiator for the high-pressure polymerization of ethylene, such as a peroxide, a hydroperoxide, or an azo compound. The oxygen used here can be not only pure oxygen, which is used as an effective catalyst, but can also be in the form of air. A mixture of two or more types of free radical-forming catalyst, or a mixture of a free radical-forming catalyst and oxygen, can be used as the polymerization initiator.

Detailed discussions of polymerization regulators are given in a number of publications (such as P. Ehlich and G.A. Mortimer, *Advances in Polymer Science*, Vol. 7, pp. 414-421 (1970/1971), Spring-Verlag), but examples of compounds that can be used favorably include methanol, ethanol, and other such alcohols, propylene, butene-1, and other such aliphatic hydrocarbons, and propionaldehyde, *n*-butyraldehyde, and other such aldehydes. When a copolymer with a low molecular weight is to be manufactured, a polymerization regulator with a large chain transfer coefficient should, of course, be used.

A fuel oil with which the additive of the present invention can be used effectively is an intermediate fraction fuel oil whose boiling point range is between 120 and 500°C, and is a fuel oil with a narrow boiling point range in which the difference between the 20% distillation temperature and the 90% distillation temperature is less than 100°C. A fuel oil with which said additive is particularly effective is one whose 90% distillation temperature is 360°C or lower, an example of which is light oil.

The clogging resistance of the fuel oil was evaluated by means of a cold filter plugging point (CFPP) test. A detailed introduction to the CFPP test is given in the *Journal of the Petroleum Society*, Vol. 20, No. 6, pp. 530-533, 1977.

When the copolymer of the present invention is added in an amount of 0.001 to 1.0 wt% to a fuel oil with a narrow boiling point range, an improvement in low temperature clogging resistance that could not be achieved with the copolymers known in the past can be effectively achieved.

The copolymer of the present invention can be used alone as the sole additive, or it can be used together with other additives, such as pour point depressants, anti-rust agents, antioxidants, water separation agents, anti-sludge agents, and the like.

The present invention will now be described in further detail through typical practical examples.

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M 1 1 - 0 0 - 0 0*Manufacturing Example 1*

Continuous polymerization was performed using an agitated tank type of reactor with an internal volume of 1.5 L. Ethylene (32 kg/hr), vinyl butyrate (16 kg/hr, used as the vinyl carboxylate), and propylene (7.0 kg/hr, used as a chain transfer agent) were compressed at 1500 kg/cm² and preheated to 100°C in a preheating zone, after which these components were supplied to the reactor. *t*-Butyl peroxyisopropyl carbonate was used as a polymerization catalyst. This catalyst was dissolved to a concentration of 100 g/L in *n*-hexane, after which the resulting solution was compressed at 1500 kg/cm² and supplied to the reactor at a rate of 0.25 L/hr. The maximum reaction temperature was controlled to 250°C.

The vinyl butyrate content of the resulting copolymer was 9.5 mol%, there were 9.2 alkyl branches, and the number average molecular weight was 3500.

Manufacturing Examples 2 through 7

Polymerization was performed by the same method and using the same reactor as in Manufacturing Example 1. The detailed polymerization conditions are given in Table 1, and the various properties of the copolymers thus obtained are given in Table 2.

Manufacturing Examples 8 through 10 (Comparative)

For the sake of comparison, polymerization was performed in the same manner as in Manufacturing Examples 2 through 7 under the polymerization conditions shown in Table 1. The properties of the copolymers thus obtained are given in Table 2.

The vinyl carboxylate content in the copolymers shown in Table 2 was determined by the method set forth in JIS K 6730, in which hydrolysis is followed by the titration of the freed carboxylic acids.

When vinyl butyrate and vinyl acetate were both used, the content of each was determined by using gas chromatography to measure the molar ratio of the carboxylic acids freed after hydrolysis.

Table 1

	Reaction temp. (°C)	Reaction pressure (kg/cm ²)	Ethylene supply amount (kg/hr)	Vinyl caproate		Chain transfer agent Type	Supply rate (kg/hr)	Polymerization catalyst Type	Supply rate (kg/hr)
				Type	Supply rate (kg/hr)				
Mfg. Ex. 1	250	1500	32	vinyl butyrate	16	propylene	7.0	perbutyl I	25
Mfg. Ex. 2	250	1500	32	vinyl butyrate	16	propylene	2.6	perbutyl I	10
Mfg. Ex. 3	250	1500	32	vinyl butyrate	16	propionaldehyde	1.1	perbutyl I	12
Mfg. Ex. 4	250	1500	32	vinyl butyrate	7.0	propylene	3.0	perbutyl I	10
Mfg. Ex. 5	250	1500	32	vinyl butyrate	8.5	propionaldehyde	0.3	perbutyl I	25
Mfg. Ex. 6	250	1500	32	vinyl butyrate	5.5	propylene	7.0	perbutyl I	10
Mfg. Ex. 7	250	1500	32	vinyl acetate	32	propylene	7.0	perbutyl I	25
Mfg. Ex. 8	250	1500	32	vinyl caprylate	32	propylene	7.0	perbutyl I	25
Mfg. Ex. 9	250	1500	32	vinyl butyrate	32	propylene	5.0	perbutyl I	18
Mfg. Ex. 10	250	1500	32	vinyl butyrate	32	propionaldehyde	0.8	perbutyl IB	0.4
				vinyl acetate	32	propylene	7.0	perbutyl I	25

Note: Perbutyl I: *t*-butyl peroxyisopropyl carbonatePerbutyl IB: *t*-butyl peroxyisopropyl butyrate

Manufacturing Examples 8 through 10 are comparative examples

Table 2

	Vinyl carboxylate		Alkyl branches (no./100 methylene groups)	Number average molecular weight
	Type	Content (mol%)		
Mfg. Ex. 1	vinyl butyrate	9.5	9.2	3500
Mfg. Ex. 2	vinyl butyrate	9.4	8.5	2300
Mfg. Ex. 3	vinyl butyrate	10.1	6.9	4600
Mfg. Ex. 4	vinyl butyrate	4.6	8.7	2400
Mfg. Ex. 5	vinyl butyrate	5.5	9.5	3600
	vinyl acetate	5.0		
Mfg. Ex. 6	vinyl butyrate	1.4	9.7	3500
	vinyl acetate	8.9		
Mfg. Ex. 7	vinyl caprylate	4.5	9.4	3400
Mfg. Ex. 8	vinyl butyrate	10.3	7.0	5500
Mfg. Ex. 9	vinyl butyrate	10.5	4.1	3700
Mfg. Ex. 10	vinyl acetate	11.8	9.8	3300

Manufacturing Examples 8 through 10 are comparative examples

Practical Example 1

In order to examine the merits of the copolymers of the present invention, the copolymer of Manufacturing Example 1 was dissolved at a concentration of 0.05 wt% in a fuel oil A, whose CFPP was -6°C, whose 90% distillation temperature was 290°C, and whose difference between the 90% distillation temperature and the 20% distillation temperature was 75°C, and in a fuel oil B, whose CFPP was -2°C, whose 90% distillation temperature was 365°C, and whose difference between the 90% distillation temperature and the 20% distillation temperature was 90°C, and the CFPP [of these solutions] was measured. When [the copolymer] was added to fuel oil A, the CFPP was -11°C, and when added to fuel oil B, the CFPP was -10°C.

Practical Examples 2 through 7

Using the fuel oils A and B used in Practical Example 1, the copolymers of Manufacturing Examples 2 through 7 were dissolved at a concentration of 0.05 wt%, and the CFPP was measured. These results are given in Table 3.

Comparative Examples 1 through 3

Using the fuel oils A and B used in Practical Example 1, the copolymers of Manufacturing Examples 8 through 10 were dissolved at a concentration of 0.05 wt%, and the CFPP was measured. These results are given in Table 3.

Table 3

	Copolymer	Fuel oil A	Fuel oil B
Practical Ex. 1	copolymer of Mfg. Ex. 1	-11°C	-10°C
Practical Ex. 2	copolymer of Mfg. Ex. 2	-12°C	-10°C
Practical Ex. 3	copolymer of Mfg. Ex. 3	-8°C	-7°C
Practical Ex. 4	copolymer of Mfg. Ex. 4	-9°C	-8°C
Practical Ex. 5	copolymer of Mfg. Ex. 5	-8°C	-8°C
Practical Ex. 6	copolymer of Mfg. Ex. 6	-7°C	-7°C
Practical Ex. 7	copolymer of Mfg. Ex. 7	-8°C	-8°C
Comp. Ex. 8	copolymer of Mfg. Ex. 8	-6°C	-5°C
Comp. Ex. 9	copolymer of Mfg. Ex. 9	-6°C	-5°C
Comp. Ex. 10	copolymer of Mfg. Ex. 10	-6°C	-4°C